OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-93-1-0780

PR Number 98PR03897-00

Title of GRANT or CONTRACT
RESPONSIVE AMPHIPHILIC POLYMERS AND MEMBRANES FOR WATER REMEDIATION

Name of Principal Investigator
Charles L. McCormick

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The University of Southern Mississippi

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Date Submitted
July 10, 1998

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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

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Principal Investigator: Charles L. McCormick
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a. Number of papers submitted to refereed journals, but not published: 2
b. + Number of papers published in refereed journals (for each, provide a complete citation): 7
c. + Number of books or chapters submitted, but not yet published: 0
d. + Number of books or chapters published (for each, provide a complete citation): 0
e. + Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 6
f. Number of patents filed: 0
g. + Number of patents granted (for each, provide a complete citation): 0
h. + Number of invited presentations (for each, provide a complete citation): 7
i. + Number of submitted presentations (for each, provide a complete citation): 4
j. + Honors/Awards/Prizes for contract/grant employees (list attached): 1
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number: 7
Graduate Students: 6
Post-Doctoral Associates: 1
including the number of,
Female Graduate Students: 1
Female Post-Doctoral Associates: 0
the number of
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 0
and, the number of
Asian Graduate Students: 0
Asian Post-Doctoral Associates: 1
l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)
Gillette Research Foundation ($80,000/year)
Nalco Corporation ($30,000/year)
Calgon Corporation ($10,000/year)

B. Published Papers in Refereed Journals

Water-Soluble Polymers. 69. pH- and Electrolyte-Responsive Copolymers of Acrylamide and the Zwitterionic Monomer 4-(2-Acrylamido-2-methylpropyldimethylammonio) Butanoate: Synthesis and Solution Behavior. Erich E. Kathmann, Leslie A. White, and Charles L. McCormick, *Polymer* **38** (4), 871 (1997).

Water-Soluble Polymers. 70. Effects of Methylene versus Propylene Spacers in the pH and Electrolyte Responsiveness of Zwitterionic Copolymers Incorporating Carboxybetaine Monomers. Erich E. Kathmann, Leslie A. White, and Charles L. McCormick, *Polymer* **38** (4), 879 (1997).

Water-Soluble Polymers. 71. pH Responsive Behavior of Terpolymers of Sodium Acrylate, Acrylamide, and the Zwitterionic Monomer 4-(2-Acrylamido-2-methylpropyldimethylammonio) Butanoate. Erich E. Kathmann and Charles L. McCormick, *Journal of Polymer Science: Part A: Polymer Chemistry* **35**, 231 (1997).

Water-Soluble Polymers. 72. Synthesis and Solution Behavior of Responsive Copolymers of Acrylamide and the Zwitterionic Monomer 6-(2-Acrylamido-2-methylpropyldimethylammonio) Hexanoate. Erich E. Kathmann and Charles L. McCormick, *Journal of Polymer Science: Part A: Polymer Chemistry* **35**, 243 (1997).

Water-Soluble Polymers. 73. Electrolyte and pH-Responsive Zwitterionic Copolymers of 4-(2-Acrylamido-2-methylpropyldimethylammonio) Butanoate with 3-(2-Acrylamido-2-methylpropyldimethylammonio) Propanesulfonate. Erich E. Kathmann, Leslie A. White, and Charles L. McCormick, *Macromolecules* **30**, 5397 (1997).

Water-Soluble Polymers. 74. pH Responsive Microdomains in Labeled N-Octylamide-Substituted Poly(Sodium Maleate-*alt*-Ethyl Vinyl Ethers) I: Synthesis, Steady-State Fluorescence, and Non-Radiative Energy Transfer Studies. Yuxin Hu, Geoffrey L. Smith, Michael F. Richardson, and Charles L. McCormick, *Macromolecules* **30**, 3526 (1997).

Water-Soluble Polymers. 75. Responsive Microdomains in Labeled N-Octylamide-Substituted Poly(Sodium Maleate-*alt*-Ethyl Vinyl Ethers) II: Transient Fluorescence and Time-Resolved Fluorescence Anisotropy Studies. Yuxin Hu, Scott Armentrout, and Charles L. McCormick, *Macromolecules* **30**, 3536 (1997).

E. Published Papers in Non-Refereed Journals

Cyclocopolymerization of Novel Diallyl Quaternary Ammonium Monomers to Yield Ordered Structures in Aqueous Media. Yuxin Hu and Charles L. McCormick, *Polymer Preprints* **38** (1), 97 (1997).

The Synthesis and Solution Behavior of Zwitterionic Cyclocopolymers Containing a Novel Sulfobetaine Monomer. R. Scott Armentrout and Charles L. McCormick, *Polymer Preprints* **39** (1), 617 (1998).

Synthesis and Characterization of Novel Hydrophobically Modified Associative Polymers Utilizing Micellar Polymerization Techniques. Geoffrey L. Smith and Charles L. McCormick, *Polymer Preprints* **39** (1), 310 (1998).

Synthesis and Characterization of Monomeric and Polymeric Vesicles Formed by N, N-Diallyl-N, N-dialkylammonium Chloride Monomers. Michael F. Richardson and Charles L. McCormick, *Polymer Preprints* **39** (1), 312 (1998).

Effects of Varying pH on the Drag Reduction Performance of a pH Responsive Copolymer. Martin E. Cowan, Richard Nause, Roger D. Hester, and Charles L. McCormick, *Polymer Preprints* **39** (1), 343 (1998).

Sequestration of a Model Water Foulant Driven by a Unimer to Multimer Transition of a Triblock Polymeric Surfactant. R. Scott Armentrout, Michael F. Richardson, and Charles L. McCormick, *Polymer Preprints* **39** (1), 349 (1998).

H. Invited Presentations

Cyclocopolymerization of Novel Diallyl Quaternary Ammonium Monomers to Yield Ordered Structures in Aqueous Media. Yuxin Hu and Charles L. McCormick, National ACS Meeting, San Francisco, CA (April 13-17, 1997)

Polymers for Application in Petroleum Oil Recovery. Caracas, Venezuela (July 9-19, 1997).

Polyampholyte and other Zwitterionic Systems. BASF, Germany (August 1, 1997).

Zwitterionic Cyclocopolymers: A New Class of Polyampholytes Containing Sulfobetaine and Carboxybetaine Moieties. R. Scott Armentrout, Yuxin Hu, Michael F. Richardson, and Charles L. McCormick, Fifth Chemical Congress of North America, Cancun, Mexico (November 11-15, 1997).

Greywater Remediation: Development of Remediative Processes Utilizing Colloidal Enhanced Ultrafiltration with Hollow Fiber Membranes. R. Scott Armentrout, and Charles L. McCormick, Spring Meeting of the American Institute of Chemical Engineers, Session 71, New Developments in Membrane Separations, New Orleans, LA (March 10, 1998).

The Synthesis and Solution Behavior of Zwitterionic Cyclocopolymers Containing a Novel Sulfobetaine Monomer. R. Scott Armentrout and Charles L. McCormick, National ACS Meeting, Specialty Monomers and their Polymers, Dallas, TX (March 27-April 3, 1998).

Structurally Tailored Amphiphilic Polymers with Modes of Hydrophobic Association in Aqueous Media. Charles McCormick and Geoffrey Smith, ICI North American Science & Technology Conference, Strongsville, OH (April 20-22, 1998).

I. Submitted Presentations

Stimuli-Responsive Zwitterionic Cyclocopolymers: Synthesis and Solution Behavior of a Novel Class of Polyampholytes. R. Scott Armentrout, Michael F. Richardson, and Charles L. McCormick, Mississippi Academy of Sciences, Biloxi, MS (February 22, 1998).

Greywater Remediation: Development of Remediative Processes Utilizing Colloidal Enhanced Ultrafiltration with Hollow Fiber Membranes. R. Scott Armentrout and Charles L. McCormick, Spring Meeting of the American Institute of Chemical Engineers, Session 71, New Developments in Membrane Separations, New Orleans, LA (March 10, 1998).

Wastewater Remediation: Utilization of Environmentally Responsive Polymeric Surfactants for the Sequestration and Subsequent Release of Model Water Foulants. Scott Armentrout, Michael Richardson, and Charles L. McCormick, National ACS Meeting, Surfactant-Based Separations, Dallas, TX (March 27-April 3, 1998).

Responsive Hydrophilic Polymers. Kumamoto University, Kumamoto, Japan (1998).

J. Honors

Charles L. McCormick: Bennett Distinguished Research Professorship, University of Southern Mississippi, Hattiesburg, MS (1997-1999).

EOY Report-Part II

GRANT: N00014-93-1-0780

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Cognizant ONR Program Officer:
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e. Significant results during the last year:

During the past year our group has demonstrated that polymer enhanced ultrafiltration may be utilized to effectively remove organic foulants from a wastewater stream. This technology is an advancement of micellar enhanced ultrafiltration that is commonly found in many remediation efforts. Micellar enhanced ultrafiltration is characterized by the addition of a small molecule surfactant to the aqueous stream containing an organic foulant. The foulant is solubilized within the micellar hydrophobic core and the stream is then passed through a microporous membrane, such that most of the organic solute and surfactant remain in the retentate. Although this method often achieves high efficiencies of removing a foulant, monomeric surfactant continuously crosses the membrane into the permeate. Therefore, added surfactant is required as time progresses to maintain a critical micelle concentration. In order to circumvent this problem, we have utilized a commercially available polymeric surfactant (Pluronic F127) as the solubilization agent. In this case, the size of the surfactant is sufficiently large to prevent passage through the membrane into the permeate and the addition of surfactant to the retentate is unnecessary. We have shown that the PEO-PPO-PEO triblock copolymer will associate with model water foulants in an ultrafiltration application such that this technology may be utilized in a closed system such as that would be required on a naval vessel.

f. Summary of plans for next years work

To date, we have demonstrated that the utilization of polymeric surfactants may replace small molecule surfactants in micellar enhanced ultrafiltration applications. However, our ultimate goal is to develop environmentally responsive polymeric surfactants such that the binding of the foulant to the polymer may be controlled by changes in temperature, pH, ionic strength, etc. These systems would allow for an in situ mechanism of removing the foulant from the polymeric surfactant. We are currently involved in the synthesis and characterization of novel polymeric surfactants based on cyclopolymers of diallyl methyl amine. These polymers show pH dependent aggregation behavior in aqueous media. It is our plan to investigate the efficiency of these novel polymers in the polymer enhanced ultrafiltration application as discussed above.

Graduate Student Investigators
R. Scott Armentrout
Martin E. Cowan
Kathy M. Johnson
Garrett Poe
Geoffrey L. Smith
David Thomas

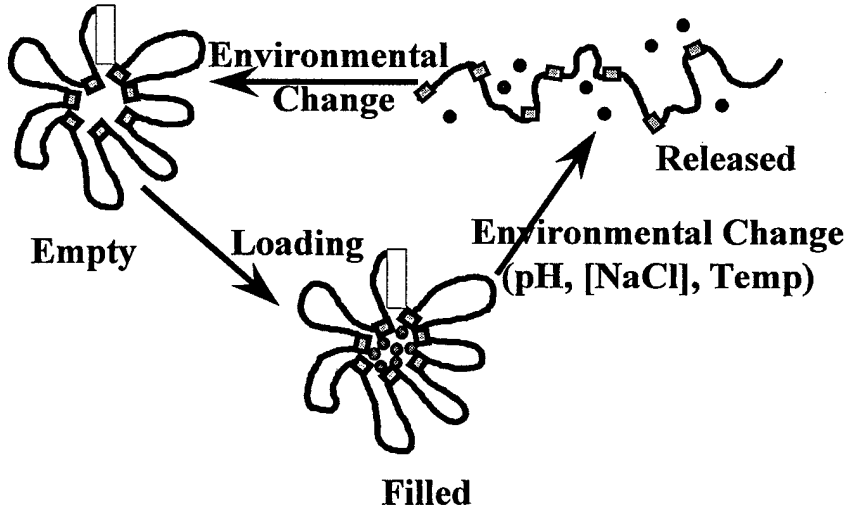
Post-Doctoral Associate
Yuxin Hu

Micellar Enhanced Ultrafiltration

University of Southern Mississippi, Hattiesburg, Mississippi

Technology Issues: Greywater remediation, design and synthesis of environmentally responsive polymeric surfactants, controled binding of water foulants within polymeric associates

Objective: Develop new technologies to remove foulants from a wastewater stream.



Approach:

•Develop structure-property relationships in the development of environmentally responsive polymeric surfactants

•Utilize polymeric surfactants in micellar enhanced ultrafiltration applications

Accomplishment:

• Demonstrated the use of commercially available polymeric surfactants in an ultrafiltration application for the removal of model water foulants

Impact:

•Polymeric surfactants utilized in an ultrafiltration application are quantitatively retained within the retentate thereby circumventing the addition of small molecule surfactants throughout the process. (A major problem in conventional micellar enhanced ultrafiltration.)

Ultrafiltration via Responsive Polymeric Surfactants

Goal: Enhanced Water Remediation

- Efficient Foulant Rejection
- High Permeate Flux
- Stimuli Reversible Sequestration

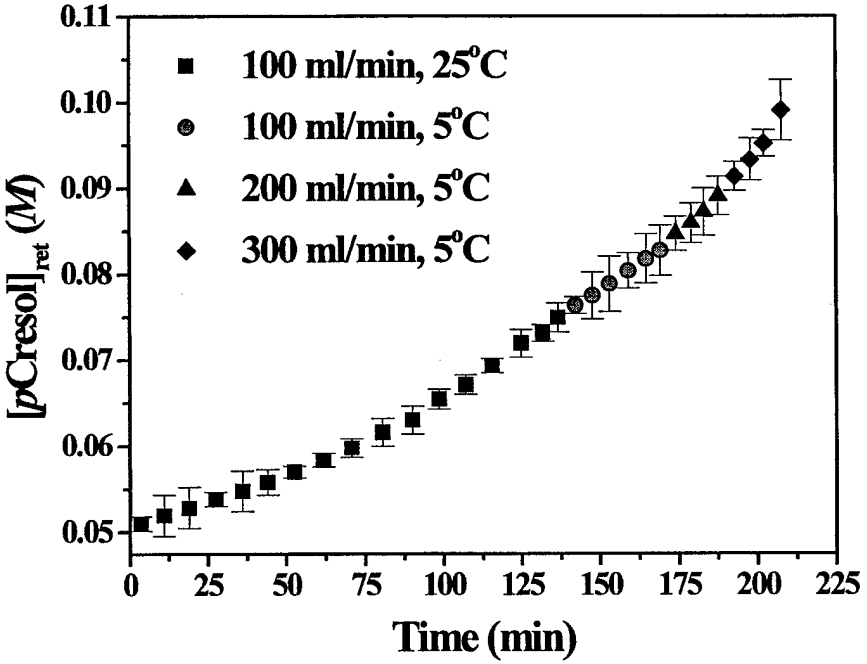
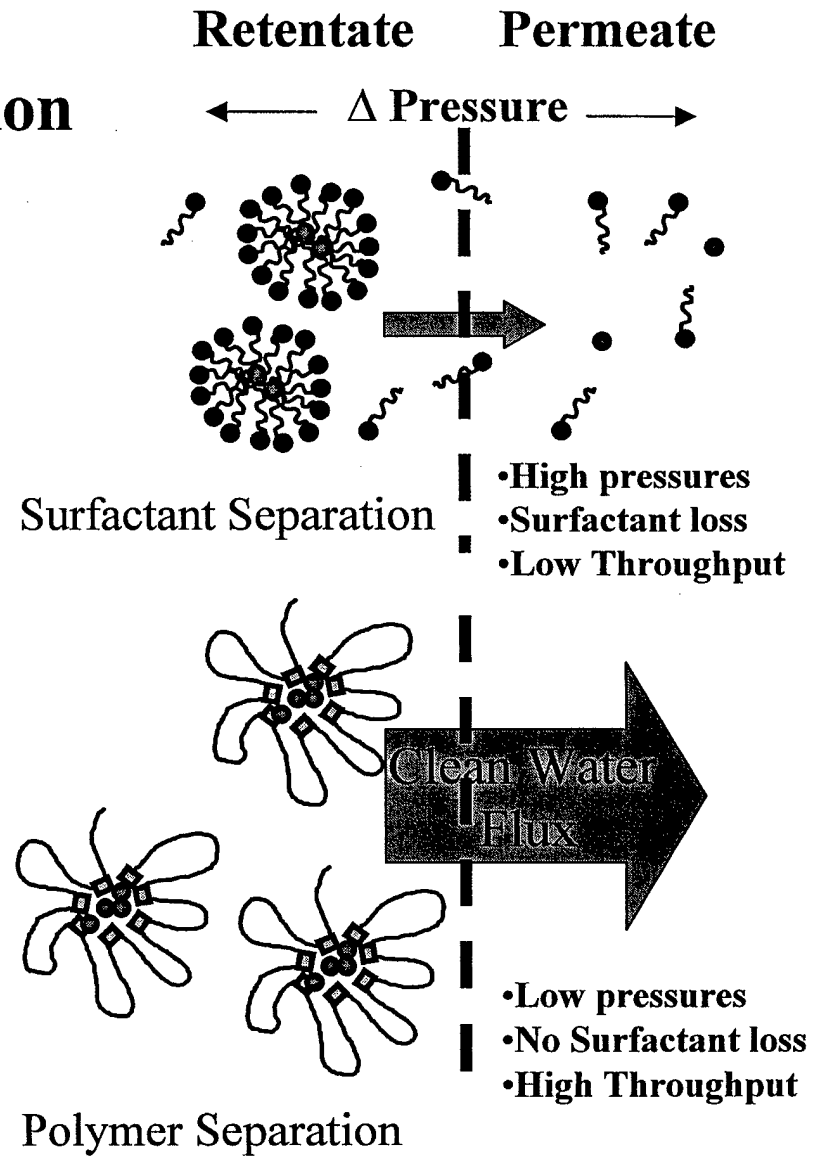


Figure 1. Plot illustrating capture and concentration of foulant, *p*-cresol, with time allowing passage of cleaned water. (Retentate flow rates are shown in legend.)



Hollow Fiber Remediation Filter